

WHAT IS CLAIMED IS:

1. An electrode active material comprising a compound of the formula



wherein

- (a) A is selected from the group consisting of Li, Na, K, and mixtures thereof, and $0 < a \leq 8$;
- (b) M comprises one or more metals, comprising at least one metal which is capable of undergoing oxidation to a higher valence state, and $1 \leq b \leq 3$;
- (c) XY_4 is selected from the group consisting of $X'O_{4-x}Y'_x$, $X'O_{4-y}Y'_{2y}$, $X''S_4$, and mixtures thereof, where X' is P, As, Sb, Si, Ge, S, and mixtures thereof; X'' is P, As, Sb, Si, Ge and mixtures thereof; Y' is halogen; $0 \leq x < 3$; and $0 < y < 4$; and $0 < c \leq 3$;
- (d) Z is OH, halogen, or mixtures thereof, and $0 < d \leq 6$; and

wherein M, X, Y, Z, a, b, c, d, x and y are selected so as to maintain electroneutrality of said compound.

2. An electrode active material according to Claim 1, wherein $c = 1$.
3. An electrode active material according to Claim 2, wherein $0.1 \leq a \leq 3$, and $0.1 \leq d \leq 3$.

4. An electrode material according to Claim 3, wherein $1 \leq a \leq 3$, and $1 \leq d \leq 3$.
5. An electrode active material according to Claim 2, wherein said active material has an olivine structure.
6. An electrode active material according to Claim 1, wherein $c = 3$.
7. An electrode active material according to Claim 6, wherein $2 \leq a \leq 6$, and $2 \leq d \leq 6$.
8. An electrode active material according to Claim 7, wherein $3 \leq a \leq 6$, and $3 \leq d \leq 6$.
9. An electrode active material according to Claim 6, wherein said active material has a NASICON structure.
10. An electrode active material according to Claim 1, wherein A comprises Li.
11. An electrode active material according to Claim 1, wherein A is selected from the group consisting of Na, K, mixtures thereof, and mixtures thereof with Li.
12. An electrode active material according to Claim 11, wherein A comprises Na.

13. An electrode active material according to Claim 1, wherein M comprises two or more transition metals from Groups 4 to 11 of the Periodic Table.
14. An electrode active material according to Claim 13, wherein said transition metals are selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Zr, Ti, and Cr.
15. An electrode active material according to Claim 1, wherein M comprises $M'_{1-m}M''_m$, where M' is at least one transition metal from Groups 4 to 11 of the Periodic Table; M'' is at least one element which is from Group 2, 3, 12, 13, or 14 of the Periodic Table; and $0 < m < 1$.
16. An electrode active material according to Claim 15, wherein M' is selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Zr, Ti, Cr, and mixtures thereof.
17. An electrode active material according to Claim 16, wherein M' is selected from the group consisting of Fe, Co, Mn, Cu, V, Cr, and mixtures thereof.

18. An electrode active material according to Claim 15, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, Al, and mixtures thereof.
19. An electrode active material according to Claim 18, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Ba, Al, and mixtures thereof.
20. An electrode active material according to Claim 1, wherein X' comprises As, Sb, Si, Ge, S, and mixtures thereof; and X'' comprises As, Sb, Si, Ge and mixtures thereof.
21. An electrode active material according to Claim 20, wherein X' comprises Si, and X'' comprises Si.
22. An electrode active material according to Claim 1, wherein XY₄ is selected from the group consisting of X'O_{4-x}Y'_x, X'O_{4-y}Y'_{2y}, X''S₄, and mixtures thereof, where X' is P and X'' is P; and 0 < x < 3; and 0 < y < 4.

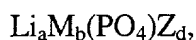
23. An electrode active material according to Claim 1, wherein XY_4 is selected from the group consisting of $X'O_{4-x}Y'_x$, $X'O_{4-y}Y'_{2y}$, $X''S_4$, and mixtures thereof, where X' is P, As, Sb, Si, Ge, S, and mixtures thereof; X'' is P, As, Sb, Si, Ge and mixtures thereof; Y' is halogen; $0 < x < 3$; and $0 < y < 4$.
24. An electrode active material according to Claim 1, wherein Y' is F.
25. An electrode active material according to Claim 1, wherein XY_4 comprises $X''S_4$.
26. An electrode active material according to Claim 1, wherein Z comprises F.
27. An electrode active material according to Claim 26, wherein Z is F.
28. An electrode active material according to Claim 27, wherein XY_4 is selected from the group consisting of $X'O_{4-x}Y'_x$, $X'O_{4-y}Y'_{2y}$, $X''S_4$, and mixtures thereof, where X' is P and X'' is P; and $0 < x < 3$; and $0 < y < 4$.
29. An electrode active material according to Claim 1, wherein Z comprises OH.

30. An electrode active material according to Claim 29, wherein X' is P, and X'' is P.

31. An electrode active material according to Claim 1, wherein X comprises Br or Cl.

32. An electrode active material according to Claim 31, wherein X' is P, and X'' is P.

33. An electrode active material comprising a compound of the formula



wherein

(a) $0.1 < a \leq 4$;

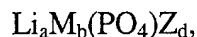
(b) M is $\text{M}'_{1-m}\text{M}''_m$, where M' is at least one transition metal from Groups 4 to 11 of the Periodic Table; M'' is at least one element which is from Group 2, 3, 12, 13, or 14 of the Periodic Table and $0 < m < 1$, and $1 \leq b \leq 3$; and

(c) Z comprises halogen, and $0.1 < d \leq 4$; and

wherein M, Z, a, b, and d are selected so as to maintain electroneutrality of said compound.

34. An electrode active material according to Claim 33, wherein M' is selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Zr, Ti, Cr, and mixtures thereof.

35. An electrode active material according to Claim 34, wherein M' is selected from the group consisting of Fe, Co, Mn, Cu, V, Cr, and mixtures thereof.
36. An electrode active material according to Claim 33, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, Al, and mixtures thereof.
37. An electrode active material according to Claim 36, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Ba, Al, and mixtures thereof
38. An electrode active material according to Claim 33, wherein Z comprises F.
39. An electrode active material comprising a compound of the formula



wherein

- (a) $0.1 < a \leq 4$;
- (b) M is one or more metals, comprising at least one metal which is capable of undergoing oxidation to a higher valence state, and $1 \leq b \leq 3$; and
- (c) Z is OH or a mixture of OH and halogen, and $0.1 < d \leq 4$; and

wherein M, Z, a, b, and d are selected so as to maintain electroneutrality of said compound.

40. An electrode active material according to Claim 37, wherein M comprises $M'_{1-m}M''_m$, where M' is at least one transition metal from Groups 4 to 11 of the Periodic Table; M'' is at least one element which is from Group 2, 3, 12, 13, or 14 of the Periodic Table; and $0 < m < 1$.
41. An electrode active material according to Claim 40, wherein M' is selected from the group consisting of Fe, Co, Mn, Cu, V, Zr, Ti, Cr, and mixtures thereof.
42. An electrode active material according to Claim 41, wherein M' is selected from the group consisting of Fe, Co, Mn, Cu, V, Cr, and mixtures thereof.
43. An electrode active material according to Claim 40, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, Al, and mixtures thereof.
44. An electrode active material according to Claim 43, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Ba, Al, and mixtures thereof.

45. An electrode active material comprising a compound of the formula



wherein

- (b) M is $\text{M}'_{1-b}\text{M}''_b$, where M' is at least one transition metal from Groups 4 to 11 of the Periodic Table; and M'' is at least one element which is from Group 2, 3, 12, 13, or 14 of the Periodic Table, and $0 \leq b < 1$; and

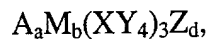
- (c) Z comprises halogen, and $0.1 < d \leq 2$; and

wherein M, Z, b, and d are selected so as to maintain electroneutrality of said compound.

46. An electrode active material according to Claim 45, wherein M' is selected from the group consisting of Fe, Co, Mn, Cu, V, Zr, Ti, Cr, and mixtures thereof.
47. An electrode active material according to Claim 46, wherein M' is selected from the group consisting of Fe, Co, Mn, Cu, V, Cr, and mixtures thereof.
48. An electrode active material according to Claim 45, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, Al, and mixtures thereof.
49. An electrode active material according to Claim 48, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Ba, Al, and mixtures thereof.

50. An electrode active material according to Claim 45, wherein Z comprises F.
51. An electrode active material according to Claim 45, of the formula $\text{Li}_2\text{MPO}_4\text{F}$, wherein M is selected from the group consisting of Ti, V, Cr, Mn, Fe, Co, Cu, Zn, or mixtures thereof.
52. An electrode active material according to Claim 51, wherein M is Fe, Co, Mn, or mixtures thereof.
53. An electrode active material according to Claim 52, of the formula $\text{Li}_2\text{CoPO}_4\text{F}$ or $\text{Li}_2\text{FePO}_4\text{F}$.
54. An electrode active material according to Claim 45, wherein M' is Fe or Co, M'' is Mg, and X is F.
55. An electrode active material according to Claim 54, wherein M' is Fe.
56. An electrode active material according to Claim 55, of the formula $\text{Li}_2\text{Fe}_{0.9}\text{Mg}_{0.1}\text{PO}_4\text{F}$.

57. An electrode active material comprising a compound of the formula



wherein

- (a) A is selected from the group consisting of Li, Na, K, and mixtures thereof, and $2 \leq a \leq 8$;
- (b) M comprises one or more metals, comprising at least one metal which is capable of undergoing oxidation to a higher valence state, and $1 \leq b \leq 3$;
- (c) XY_4 is selected from the group consisting of $X'O_{4-x}Y'_x$, $X'O_{4-y}Y'_{2y}$, $X''S_4$, and mixtures thereof, where X' is P, As, Sb, Si, Ge, S, and mixtures thereof; X'' is P, As, Sb, Si, Ge and mixtures thereof; Y' is halogen; $0 \leq x < 3$; and $0 < y < 4$;
- (d) Z is OH, halogen, or mixtures thereof, and $0 < d \leq 6$; and

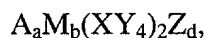
wherein M, X, Y, Z, a, b, d, x and y are selected so as to maintain electroneutrality of said compound.

- 58. An electrode active material according to Claim 57, wherein A comprises Li.
- 59. An electrode active material according to Claim 57, wherein A comprises Na, K, or mixtures thereof.

60. An electrode active material according to Claim 57, wherein M comprises two or more transition metals from Groups 4 to 11 of the Periodic Table.
61. An electrode active material according to Claim 60, wherein said transition metals are selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Zr, Ti, and Cr, and mixtures thereof.
62. An electrode active material according to Claim 57, wherein M comprises $M'_{1-m}M''_m$, where M' is at least one transition metal from Groups 4 to 11 of the Periodic Table; M'' is at least one element which is from Group 2, 3, 12, 13, or 14 of the Periodic Table; and $0 < m < 1$.
63. An electrode active material according to Claim 62, wherein M' is selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Zr, Ti, Cr, and mixtures thereof.
64. An electrode active material according to Claim 63, wherein M' is selected from the group consisting of Fe, Co, Mn, Cu, V, Cr, and mixtures thereof.

65. An electrode active material according to Claim 62, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, Al, and mixtures thereof.
66. An electrode active material according to Claim 65, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Ba, Al, and mixtures thereof
67. An electrode active material according to Claim 57, wherein XY₄ is PO₄.
68. An electrode active material according to Claim 57, wherein X' comprises As, Sb, Si, Ge, S, and mixtures thereof; X'' comprises As, Sb, Si, Ge and mixtures thereof; and $0 < x < 3$.
69. An electrode active material according to Claim 57, wherein Z comprises F.
70. An electrode active material according to Claim 57, wherein Z comprises OH.

71. An electrode active material comprising an active material of the formula



wherein

- (a) A is selected from the group consisting of Li, Na, K, and mixtures thereof, and $0.1 < a \leq 6$;
- (b) M comprises one or more metals, comprising at least one metal which is capable of undergoing oxidation to a higher valence state, and $1 \leq b \leq 3$;
- (c) XY_4 is selected from the group consisting of $X'O_{4-x}Y'_x$, $X'O_{4-y}Y'_{2y}$, $X''S_4$, and mixtures thereof, where X' is P, As, Sb, Si, Ge, S, and mixtures thereof; X'' is P, As, Sb, Si, Ge and mixtures thereof; Y' is halogen; $0 \leq x < 3$; and $0 < y < 4$; and;
- (d) Z is OH, halogen, or mixtures thereof, and $0 < d \leq 6$; and

wherein M, X, Y, Z, a, b, d, x and y are selected so as to maintain electroneutrality of said compound.

72. An electrode active material according to Claim 71, wherein A comprises Li.
73. An electrode active material according to Claim 71, wherein A comprises Na, K, or mixtures thereof.

74. An electrode active material according to Claim 71, wherein M comprises two or more transition metals from Groups 4 to 11 of the Periodic Table.
75. An electrode active material according to Claim 74, wherein said transition metals are selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Zr, Ti, and Cr, and mixtures thereof.
76. An electrode active material according to Claim 71, wherein M comprises $M'_{1-m}M_m''$, where M' is at least one transition metal from Groups 4 to 11 of the Periodic Table; M'' is at least one element which is from Group 2, 3, 12, 13, or 14 of the Periodic Table; and $0 < m < 1$.
77. An electrode active material according to Claim 76, wherein M' is selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Zr, Ti, Cr, and mixtures thereof.
78. An electrode active material according to Claim 77, wherein M' is selected from the group consisting of Fe, Co, Mn, Cu, V, Cr, and mixtures thereof.

79. An electrode active material according to Claim 76, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, Al, and mixtures thereof.
80. An electrode active material according to Claim 79, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Ba, Al, and mixtures thereof
81. An electrode active material according to Claim 71, wherein XY₄ is PO₄.
82. An electrode active material according to Claim 71, wherein X' comprises As, Sb, Si, Ge, S, and mixtures thereof; X'' comprises As, Sb, Si, Ge and mixtures thereof; and $0 < x < 3$.
83. An electrode active material according to Claim 71, wherein Z comprises F.
84. An electrode active material according to Claim 71, wherein Z comprises OH.
85. An electrode comprising a binder; an electrically conductive carbonaceous material; and an active material of Claim 1.

86. An electrode comprising a binder; an electrically conductive carbonaceous material; and an active material of Claim 33.
87. An electrode comprising a binder; an electrically conductive carbonaceous material; and an active material of Claim 39.
88. An electrode comprising a binder; an electrically conductive carbonaceous material; and an active material of Claim 45.
89. An electrode comprising a binder; an electrically conductive carbonaceous material; and an active material of Claim 57.
90. An electrode comprising a binder; an electrically conductive carbonaceous material; and an active material of Claim 71.
91. A lithium battery comprising:
- (a) a first electrode comprising an active material according to Claim 1,
 - (b) a second electrode which is a counter-electrode to said first electrode; and
 - (c) an electrolyte between said electrodes.

92. A lithium battery of Claim 91, wherein said first electrode is a cathode, and said second electrode is an insertion anode.
93. A lithium battery of Claim 92, wherein said second electrode comprises a metal oxide, metal chalcogenide, carbon, graphite, and mixtures thereof.
94. A lithium battery comprising:
- (a) a first electrode comprising an active material according to Claim 33,
 - (b) a second electrode which is a counter-electrode to said first electrode; and
 - (c) an electrolyte between said electrodes.
95. A lithium battery comprising:
- (a) a first electrode comprising an active material according to Claim 39,
 - (b) a second electrode which is a counter-electrode to said first electrode; and
 - (c) an electrolyte between said electrodes.

96. A lithium battery comprising:

- (a) a first electrode comprising an active material according to Claim 45,
- (b) a second electrode which is a counter-electrode to said first electrode; and
- (c) an electrolyte between said electrodes.

97. A lithium battery comprising:

- (a) a first electrode comprising an active material according to Claim 57,
- (b) a second electrode which is a counter-electrode to said first electrode; and
- (c) an electrolyte between said electrodes.

98. A lithium battery of Claim 97, wherein said first electrode is a cathode, and said second electrode is an insertion anode.

99. A lithium battery of Claim 98, wherein said second electrode comprises a metal oxide, metal chalcogenide, carbon, graphite, and mixtures thereof.

100. A lithium battery comprising:

- (a) a first electrode comprising an active material according to Claim 71,
- (b) a second electrode which is a counter-electrode to said first electrode; and
- (c) an electrolyte between said electrodes.